Self-healing rubbers via supramolecular assembly

AUTHOR(S):

Leibler, Ludwik

CITATION:

Leibler, Ludwik. Self-healing rubbers via supramolecular assembly. 物性研究 2009, 91(4): 419-420

ISSUE DATE:

2009-01-20

URL:

http://hdl.handle.net/2433/142743

Self-healing rubbers via supramolecular assembly.

Ludwik Leibler

Matière Molle et Chimie (UMR 7167 CNRS-ESPCI), ESPCI ParisTech,

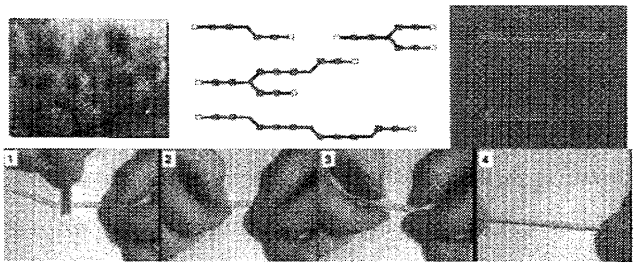
10, rue Vauquelin, 75005 Paris, France (ludwik.leibler@espci.fr)

Hydrogen bonds between molecules play an important role in determining the structure and function of biological systems. The most familiar hydrogen bond motifs are water molecules, the nucleobases found in DNA and RNA, and amino acids found in proteins. Supramolecular chemistry, an exciting research field defined as the "chemistry beyond the covalent bond", often looks for inspiration in biological world and largely employs hydrogen bonds and uses with gusto their versatility and directionality. Complex structures and materials have been synthesized by such an approach, from protein and peptide assemblies, supramolecular catalysts and molecular sensors, to stimuli responsive materials. In my talk I will focus on supramolecular polymers, small molecules which due to their non-covalent interactions and self-assembly behave in many aspects like polymer materials. The tremendous development of polymers in 20th century opened or was crucial for emergence of new cutting edge technologies and applications, from electric to entertainment (movie) industries, from airplanes to packaging, from micro- or nano- lithography to adhesives, from soft contact lenses to super-tough plastic car bumpers. We believe that a creative and efficient use of non-covalent bonds to obtain polymer-like systems should open new avenues. For example, using supramolecular assemblies of small molecules should help to better solve "easy-processing good-properties" dilemma: to be easily processable macromolecules have to be small and flow easily, but small macromolecules do not entangle and form lousy polymer materials. Incorporating, thermo-reversible non-covalent bonding moeities which are open at processing temperatures and close at working temperature should provide a way out of the dilemma. The sensitivity of such bonds to physical and chemical environment and external fields is an asset to design unique stimuli responsive materials and systems. Last but not least, covalent bonds irreversibly break when polymer material is damaged. Could a solid, e.g. a rubber, self- mend after damage? Is self-healing possible without flow?

Rubbers exhibit enormous extensibility up to several hundred percent compared with few percent for ordinary solids and ability to recover their original shape and dimensions on release of stresses. Rubber elasticity is a property of systems consisting of macromolecules either covalently cross-linked or connected in a network by physical associations such as small glassy or crystalline domains or ionic aggregates. Covalent cross-links or strong physical associations prevent flow and creep. We have designed and synthesize molecules that associate together to form both chains and cross-links via hydrogen bonds.

In principle multifunctional molecules with an average functionality higher than 2 are able of forming directional supramolecular networks and thus, behave like covalent polymer networks provided the associations of functional groups are directional and robust. Unfortunately, strong interactions between molecules favour crystallization and supramolecular networks made of "model" monodisperse identical associating molecules behave like semi-crystalline plastics, i.e., resins or fibres and not elastomer-like materials. Our solution to prevent crystallization consisted of using mixtures of multifunctional branched oligomers with a controlled distribution of shapes and lengths and equipping them with a variety of strongly associating groups. The challenge was to avoid phase separation of different species. For this purpose, we use as a starting material fatty dimer acids made from natural renewable resources, vegetable oils and available in bulk quantities and various compositions.23 They are liquid at room temperature and in contrast to other classical diacids they do not crystallize but form glasses. The glass transition can be varied by dosing the oil from which fatty diacids are made. Even more interestingly for our purpose, these starting materials can contain variable amounts of trimer acids. We thus solved the problem of synthetic availability of multitopic molecules.

However, the amount of molecular disorder brought by the presence of fatty acid trimers is not sufficient to prevent crystallization, we therefore used a two steps synthesis. In the first step, we prepared oligomeric backbones from vegetable oil fatty acid. In the second step, we provided these prepared backbones with groups capable of self-complementary and/or complementary associations. The control of molecular architecture: variety, size and distribution was of course a crucial issue.



When properly controlled, the system shows recoverable extensibility up to several hundred percent and little creep under load. In striking contrast to conventional cross-linked or thermoreversible rubbers made of macromolecules, these systems when broken or cut can be simply mended by bringing together fractured surfaces to self-heal at room temperature. Repaired samples recuperate their enormous extensibility. The process of breaking and healing can be repeated many times. These materials can be easily processed, reused and recycled. Their unique self repairing properties, the simplicity of the synthesis, the availability from renewable resources and low cost of raw ingredients, fatty acids and urea bodes well for future applications.

1. Cordier, P., Tournilhac, F., Soulié-Ziakovic, C., Leibler, L. Nature 2008, 451, 977-980
2. P.Y.W. Dankers, E.W. Meijer, Bull. Chem. Soc. Jpn. Vol. 80, No. 11, 2047–2073 (2007)